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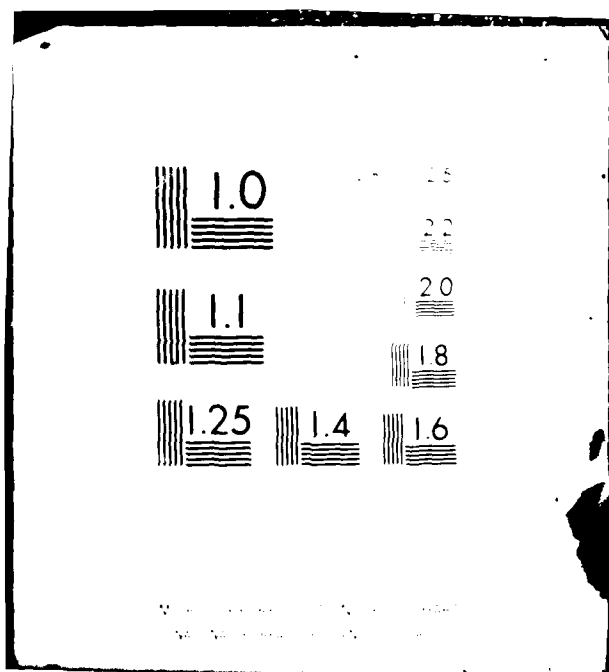
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KINETICS OF A STERICALLY HINDERED AMINE CURED EPOXY RESIN SYSTEM--ETC(U)
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KINETICS OF A STERICALLY HINDERED AMINE CURED EPOXY RESIN SYSTEM

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Aircraft and Crew Systems Technology Directorate
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Warminster, Pennsylvania 18974

2 NOVEMBER 1981

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room temperature due to the quenching of the primary amine reaction by the glassy structure and the steric hindrance of the secondary amine reaction. Apparent activation energies for these two conditions were found to be 49.4 kJ/Mol. and 49.0 kJ/Mol. respectively. The storage life at room temperature of the B-staged resin system is predicted to be at least three months based on extrapolation of the experimental kinetic data.

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KINETICS OF A STERICALLY HINDERED AMINE CURED EPOXY RESIN SYSTEM

by

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B.S. Mats. Eng., Drexel University
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OF THE REQUIREMENTS FOR THE
DEGREE OF

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KINETICS OF A STERICALLY HINDERED AMINE CURED EPOXY RESIN SYSTEM

by

LEONARD JOSEPH BUCKLEY

Submitted to the Department of Materials Science and Engineering on
May 8, 1981 in partial fulfillment of the requirements for the
Degree of Master of Science in Materials Science and Engineering

ABSTRACT

Fourier Transform Infrared Spectroscopy (FT-IR) and Torsional Braid Analysis (TBA) were used to study the reaction of an epoxy resin system cured with a sterically hindered amine. Isothermal torsional braid analysis showed the apparent activation energy to be approximately 42 kJ/Mol. The reaction kinetics were also considered from the unreacted freshly mixed condition and a partially reacted "B-staged" condition using infrared spectroscopy. The B-staged condition is unreactive and stable at room temperature due to the quenching of the primary amine reaction by the glassy structure and the steric hindrance of the secondary amine reaction. Apparent activation energies for these two conditions were found to be 49.4 kJ/Mol. and 49.0 kJ/Mol. respectively. The storage life at room temperature of the B-staged resin system is predicted to be at least three months based on extrapolation of the experimental kinetic data.

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INTRODUCTION

A current problem with resin systems used in continuous-fiber reinforced composites is their storage capability. Once the resin is mixed, it must be used immediately or stored at low temperatures in the form of a prepreg. Prepregs must typically be stored at $-18^{\circ}\text{C}(0^{\circ}\text{F})$ and at this temperature they are estimated to remain stable for approximately six months. The ideal system from a storage point of view would be a prepreg which is stable at room temperature in the B-stage and yet which retains its tack and drape. Currently no such system exists.

However, a resin system does exist which is stable at room temperature in the B-stage in a glassy condition (no tack or drape). This system (Figure 1) consists of diglycidyl ether of bisphenol-A (Dow 332) and polyglycidyl ether of orthocresol formaldehyde novolac (Ciba-Geigy 1299), hardened with 2,5-dimethyl 2,5-hexane diamine (DMHDA). Rinde and coworkers (1) have shown DGEBA/DMHDA to be stable in the B-stage at room temperature. Upon mixing at room temperature, the primary amine hydrogens react to form a linear polymer. The secondary amine hydrogens do not react at room temperature because they are much less reactive due to the steric hindrance of the nearby methyl groups. The polymer does not form a 3-dimensional structure until the secondary amine hydrogens react upon additional heating. This results in a softening and slight flow of the resin as it is being advanced to the fully cured state.

The epoxy-cresol-novolac resin (1299) was added to improve elevated temperature mechanical properties by increasing the crosslink density of the fully cured system. Due to its functionality of greater than two

(average functionality is reported to be 5.4) it is possible to develop some crosslinking with only the primary amine hydrogens reacting. However, the possibility of network formation at room temperature is considered low due to the relatively small amount of 1299 used in the formulation (14 mole percent). Previous work has shown the basic mechanism of linear polymer formation at room temperature to be retained (2).

When an epoxy cures, two principal structural transitions may occur: gelation and vitrification. Gelation corresponds to the transition from linear and branched molecules to a network structure of mathematically infinite molecular weight. Vitrification involves a transition from the liquid or rubbery state into the glassy state as a consequence of an increase in molecular weight before gelation or an increase in crosslink density after gelation. As long as the extent of cure remains below the gel point, the material is fusible and may be suitable for use as a prepreg matrix. Once the gel point is exceeded no further processing is possible.

Several authors have found that the only significant reaction of an epoxy and an amine in the absence of an accelerator is that of the amine hydrogens (3,5). The reaction seems to be more complicated when an accelerator is used; etherification reactions may complicate the simple amine addition scheme. Also, reactions such as oligomerization involving the hydroxyl and epoxy seem to be possible even in the absence of an accelerator (5).

The amine-curing reaction of epoxy resins is usually catalyzed by hydroxyl groups (6). This hydroxyl-catalyzed reaction is reported to be first order in each reactant and third order overall (7). However, the

integer-order of an epoxy curing reaction may be an oversimplification. Abalofia (8) has found the order to vary over non-integer values using DSC analysis. Therefore simple n^{th} -order kinetics with the temperature dependent rate constant given by an Arrhenius expression may be too simplified to express the entire cure reaction adequately. The present work investigates the reaction kinetics without attempting to determine the reaction order.

The storage capability of the B-staged resin system can be assessed by examining the kinetics of the curing reaction. Many authors have used infrared spectroscopy to study the curing behavior of epoxies (9-13). Signal-to-noise and resolution considerations limit rapidly scanning the entire spectrum with a dispersive instrument, and prevent the application of conventional infrared spectroscopy to the study of reactions with short half lives. With rapid-scanning Fourier Transform Infrared spectroscopy (FT-IR) the time factor limitations have been reduced and reactions with short half lives are now amenable to spectroscopic investigation (14). FT-IR is fast, which permits routine application of signal averaging techniques to develop high quality spectra, and has extensive data handling capabilities, which allow direct manipulation of the spectra. If a reactant or product exhibits an absorption free of spectral interference, the absorbance versus time plot represents a kinetic profile of this reaction species.

The epoxide group shows three characteristic infrared absorption bands. The region of the first band is small at about 1250 cm^{-1} . The regions of the two other bands are broader, the position of the maximum depending on the structure of the epoxide. These absorption bands

appear between 950 and 860 cm^{-1} (usually at 915 cm^{-1}) and between 865 and 785 cm^{-1} (generally 830 cm^{-1}). The extent of reaction can be followed by measuring the decrease in the epoxy ring absorbance as the cure proceeds.

Torsional Braid Analysis (TBA) provides a mechanical means of investigating the curing behavior of the epoxy which compliments the FT-IR technique. In this work both FTIR and TBA techniques were used to study the cure kinetics of the 332/1299/DMHDA resin system.

MATERIALS

The epoxy resin system studied consists of a stoichiometric mix of 2/3 DGEBA (Dow 332), 1/3 Novolac (Ciba 1299), and DMHDA as shown in Figure 1. The 1299 resin is a solid Novolac and may be mixed with the 332 resin by heating. The liquid 332 resin acts as a solvent for the solid 1299 resin. Upon cooling a very viscous homogeneous resin mixture is obtained. The T_g of the fully cured resin system is 144°C as determined by dynamic mechanical analysis using the DuPont 1090 DMA instrument. (The T_g was taken as the intersection between the horizontal and vertical portions of the modulus-temperature curve). The curing agent (DMHDA) is slightly volatile at the higher cure temperatures. All of the components are commercially available.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry (DSC)

A DSC scan to 200°C at 2°C/Min. of a freshly mixed sample of the resin system is shown in Figure 2a. The two exothermic peaks represent the primary and secondary amine reactions. Another DSC scan is shown in Figure 2b for the same resin system of a specimen which was kept at room temperature long enough to solidify (approximately 48 hours). This B-staged condition is not fully cured as evidenced by the single broader exotherm shown in the figure. The endothermic peak represents a melt from the solid state which then allows the reaction to proceed. This solid-state melt may be due to some crystalline melting of the linear polymer or segregated unreacted constituents. Due to this behavior, the kinetics of the curing reaction were investigated from both freshly mixed and B-staged starting conditions.

Dynamic Mechanical Analysis

Conventional Torsional Pendulum Analysis (TPA) was used to study the isothermal cure behavior of composite specimens which were prepared by impregnating graphite cloth (AS fiber; 8-harness weave) with the resin system and allowing the laminate to B-stage at room temperature. In this experiment the temperature was kept constant and the modulus and log decrement were monitored as a function of time. After softening, the cure proceeded normally, but only the final portion of the stiffness and damping plots were observable. The sensitivity of this instrument was not adequate to observe the total cure, and the time to gelation was not estimable. TPA did not yield useful kinetic data, but a similar

technique, torsional braid analysis (TBA) was attempted and proved to be more sensitive.

Isothermal TBA runs were made of the resin system at approximately 1 Hz using an automated apparatus in a helium atmosphere. The specimens were prepared by impregnating a glass braid with a resin solution in 25% methylene chloride. The methylene chloride was removed as the specimen was heated to the starting temperature. The cure of the freshly mixed resin was monitored by observing the torsional rigidity and damping as a function of time at several constant temperatures. The reader is referred to Gillham et al. (15-17) for a complete description of torsional braid analysis and its use in mapping the transformations of thermosetting systems.

The isothermal TBA run at 100°C is shown in Figure 3. At this cure temperature and also at 90°C, well defined gelation and vitrification peaks were obtained. (The total cure time was approximately 24 hours). At the higher cure temperatures no gel peaks were observed, perhaps due to loss of the volatile curing agent. The first significant decrease in the damping plot was then used to determine the apparent gel point.

Assuming arrenius kinetics, the time, t , to reach a given degree of conversion can be written:

$$t = t_0 \text{ EXP}(E_a/RT),$$

where t_0 is a constant, E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. An Arrhenius plot (assuming the conversion at the gel point is a constant) is shown

in Figure 4 using the time to gelation at different cure temperatures. The apparent activation energy from the slope of the curve is 42 kJ/Mol.

If the reaction mechanism remains the same at all temperatures, the conversion at the gel point is a constant and can be calculated (18). Using a statistical calculation for the three components, the gel point is found to be at 78% extent of reaction (19). However this assumes equal reactivity of all functional groups, which is not true for the present system. The primary amines react initially to form a linear polymer with a few scattered crosslinks due to the 1299 resin. This reaction proceeds at room temperature until quenched by vitrification. The reaction of the secondary amines requires elevated temperatures and converts the linear polymer into a crosslinked network. The polymer must be fusible and partially soluble to allow some flow if it is to be a useful prepreg resin. Fifty percent extent of reaction is estimated to be the maximum processing limit for B-staging, assuming that after this point the primary reaction has completed and the secondary (cross-linking) reaction is dominant.

Fourier Transform Infrared Spectroscopy (FT-IR)

B-staged specimens were heated in a vacuum oven at various temperatures and for various times. Potassium bromide (KBr) pellets were made and infrared spectra from 3800 to 450 cm^{-1} were collected using a Fourier Transform Spectrometer (Digilab FTS - 10M). Spectral resolution was 4 cm^{-1} and averaged over 120 scans.

In addition, thin films of the B-staged and freshly mixed resin were sandwiched between two KBr salt plates. The salt plates were mounted in a temperature-controlled cell holder with a thermocouple

inserted in a drilled cavity between the plates. Infrared spectra from 3800 to 450 cm^{-1} were recorded at one-minute intervals during the cure. This was repeated for several temperatures and for the freshly mixed condition. All spectra were taken in a nitrogen atmosphere.

A ratio indicating unreacted epoxide groups relative to the starting condition can be found by normalizing the size of the epoxide peak (915 cm^{-1}) of each scan to the aromatic peak (1510 cm^{-1}) of each scan and then dividing by the similarly normalized spectra of the starting condition.

$$A_{915}(t) = \frac{A_{915,s}}{A_{1510,s}} \frac{A_{1510,\text{ref}}}{A_{915,\text{ref}}}$$

$A_{915}(t)$ - fraction unreacted epoxide at time t

$A_{915,s}$ - specimen absorbance at 915 cm^{-1} at time t

$A_{1510,s}$ - specimen absorbance at 1510 cm^{-1} at time t

$A_{915,\text{ref}}$ - initial absorbance at 915 cm^{-1}

$A_{1510,\text{ref}}$ - initial absorbance at 1510 cm^{-1}

An example of these spectra is shown in Figure 5. The absorbances at 915 cm^{-1} versus time at various temperatures were plotted from the two starting conditions and are shown in Figures 6 and 7.

In Figure 7 (B-staged starting condition) the 100°C plot is seen to reach 45% absorbance at 915 cm^{-1} in 4 hours. The reaction at this temperature is very slow but still continues at a finite rate as evidenced

by the torsional braid analysis. The TBA run at 100°C showed the reaction to continue for approximately 24 hours (see Figure 3). The lower reaction rate at 100°C is believed to be due to vitrification and quenching of the resin system.

The 125°C and 150°C run (Figure 7) show the extent of reaction to approach 81 and 77 percent respectively in less than two hours. The 125°C run, below the maximum T_g of the fully cured system (144°C), proceeds to a significant extent of reaction before it vitrifies. The 150°C run is above the maximum T_g and does not vitrify at this temperature.

At 177°C (Figure 7) the cure temperature is significantly above the maximum T_g. The reaction initially proceeds very rapidly but then seems to slow down in a relatively short time. This may be due to the reactants degrading thermally at this elevated temperature or extensive chain crosslinking and re-vitrification.

In Figure 6 the epoxide absorbances versus time are plotted for the freshly mixed condition at three temperatures. The reactions follow the same pattern of the B-staged condition but at a slightly faster rate. This is most likely due to greater mobility of the reactants in the liquid state.

Arrhenius plots of logarithmic time to 49% conversion (51% absorbance at 915 cm⁻¹) versus reciprocal temperature are shown in Figure 8. As mentioned earlier, this conversion is believed to be the maximum at which the resin is still fusible and soluble. The activation energies calculated from the slopes of the plots of Figure 8 are similar (49.4 and 49.0 kJ/Mol.). These values agree with the work by Rinde et al. (7) in which the activation energies of the primary and secondary curing

processes were found to be identical. They are also in reasonable agreement with the activation energy found by Torsional Braid Analysis (42/kJ/Mol.).

In this work the B-staged starting condition (Figure 7) initially shows approximately 28% conversion. This was after several days at room temperature in which the resin vitrified. Extrapolation of the data in Figure 8 to room temperature yields a 3 month time to 49% conversion. The data for Figure 8 are for the rubbery or softened state after heating the B-staged resin. Gillham (16) has found the reaction rate to be slower in the glassy (Vitrified) state. Therefore, 3 months most likely represents a much shorter time to 49% conversion than what occurs in the glassy state at room temperature.

CONCLUSIONS

The results of this study show the apparent activation energies for the curing reactions to be similar, regardless of the initial condition. Using FT-IR they were found to be 49.4 kJ/Mol. (freshly mixed) and 49.0 kJ/Mol. (B-staged). Using TBA it was 42 kJ/Mol. (freshly mixed). The nature of DMHDA, which causes partial cure at room temperature by forming a glassy linear polymer, makes the cure rather complicated. Vitrification at room temperature ~~renders~~ the primary reaction. The secondary reaction requires ~~elevated~~ temperatures due to the steric hindrance of the methyl groups. ~~Softening~~, flow, and re-vitrification occurs as the resin is cured from the B-stage.

The primary reaction continues to increase the molecular weight of the system at room temperature till most of the primary amine hydrogens have reacted. The storage life therefore is the time to completion of the primary reaction which was found to be approximately three months using the experimental kinetic data. As previously mentioned, this data is based on a rubbery state after softening the B-staged resin with additional heating. (The extrapolation to room temperature used kinetics based on a rubbery condition.) The reaction rate is most likely to be slower in the glassy state at room temperature and therefore the actual storage life will be longer. To determine the actual storage life the reaction after B-staging must be monitored at room temperature for long time periods.

A glassy prepreg patch with a storage life of three months is still not adequate for field level repair of advanced composites. The

material deployment time alone may be three months. Thus, a storage life of at least one year is preferred.

Rinde et al. (17) has reported that DGEBA/DMHDA does not cross-link for up to one year if protected from moisture. Moisture plasticizes the resin allowing a faster reaction rate through increased mobility of the reactants. This may be applied to the present system if moisture absorption can be prevented. More research and development is needed in this area of stable prepreg matrix materials.

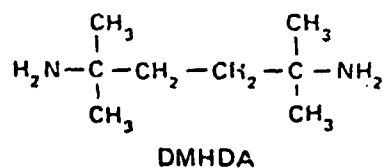
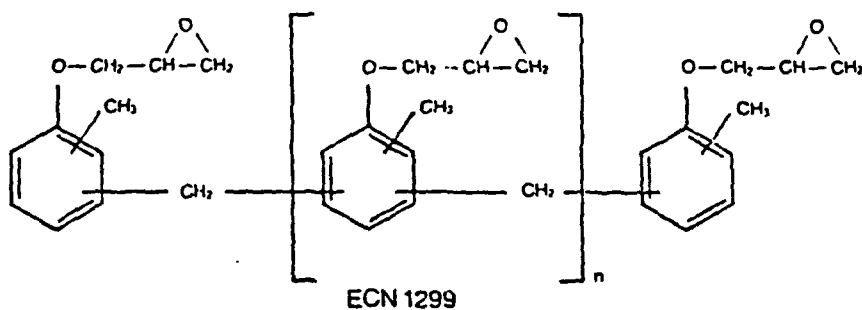
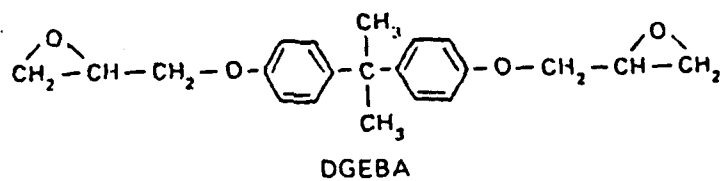


Figure 1. Components of epoxy resin system.
(Average n for ECN 1299 is 3.4)

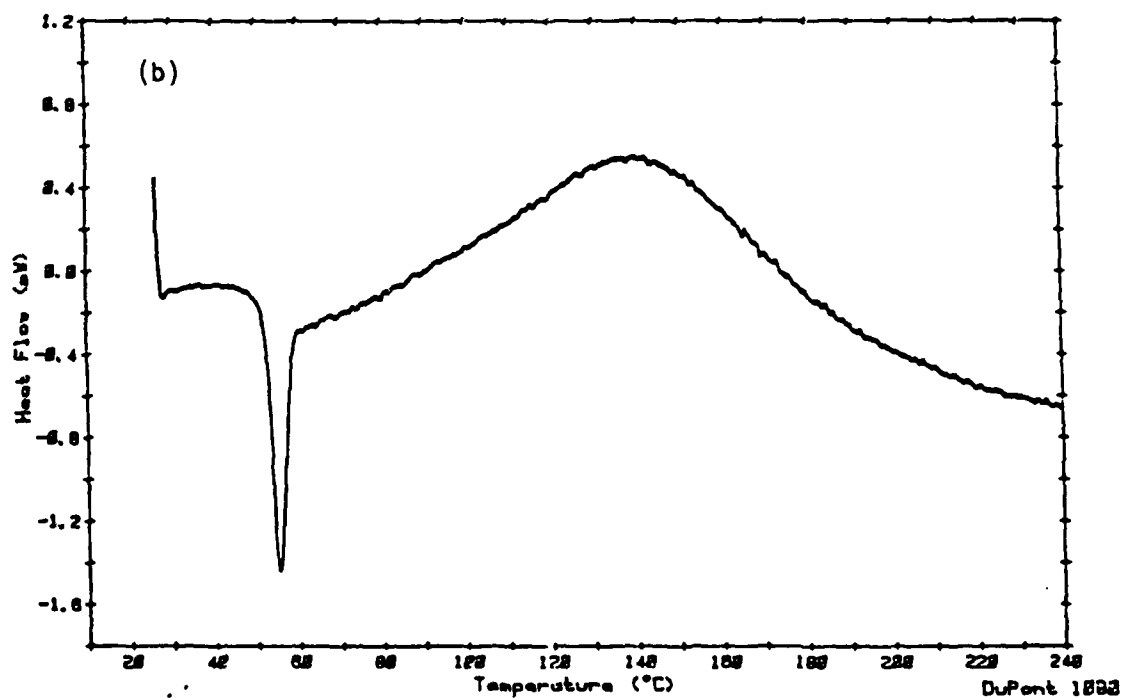
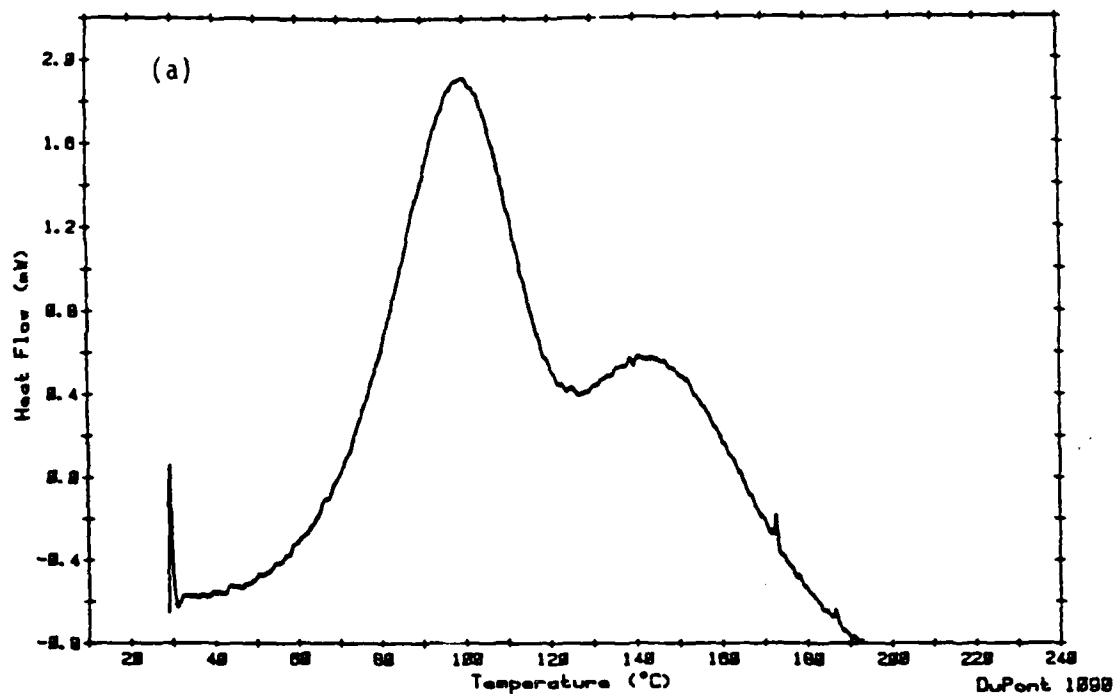


Figure 2. DSC Plots of 332/1299/DMHDA in the freshly mixed (a) and B-staged (b) condition.

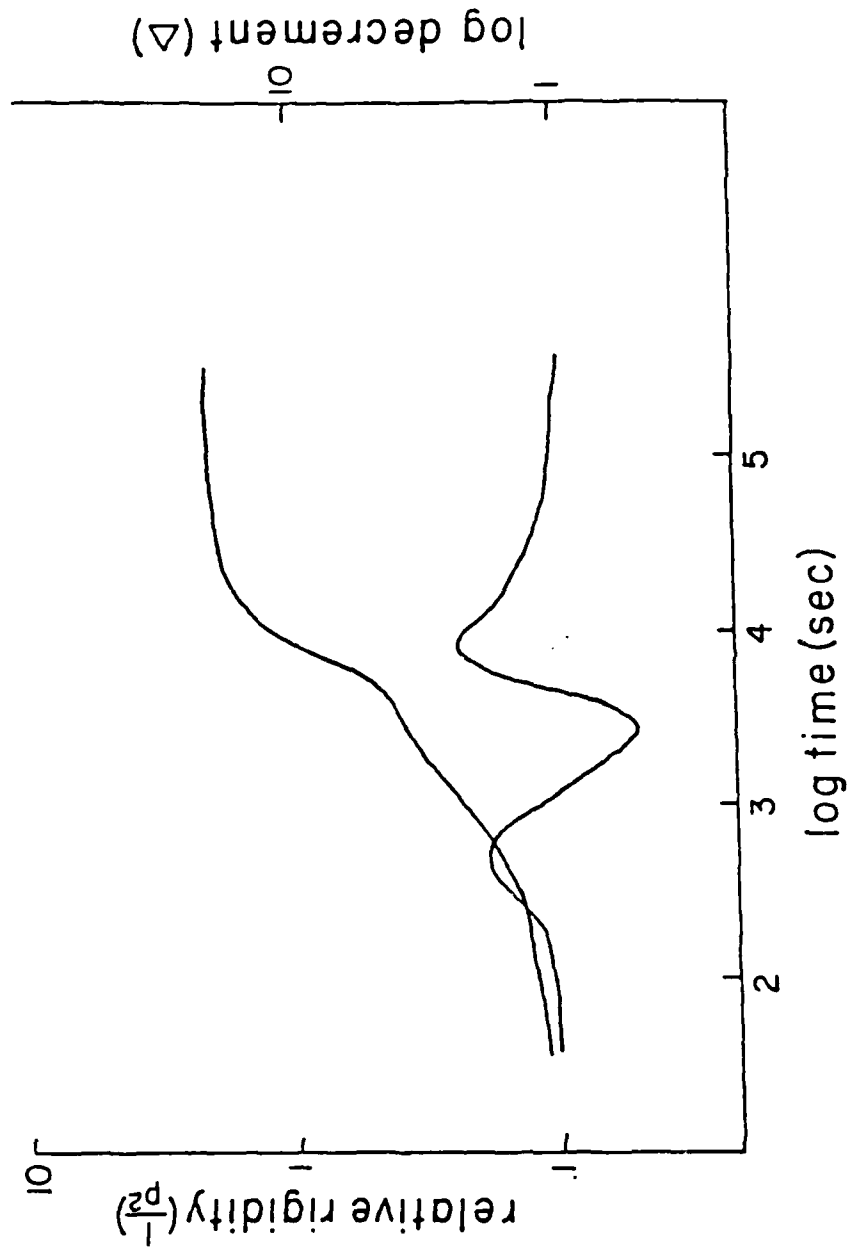


Figure 3. Isothermal TBA plot of 332/1299/DMHDA for 100°C.

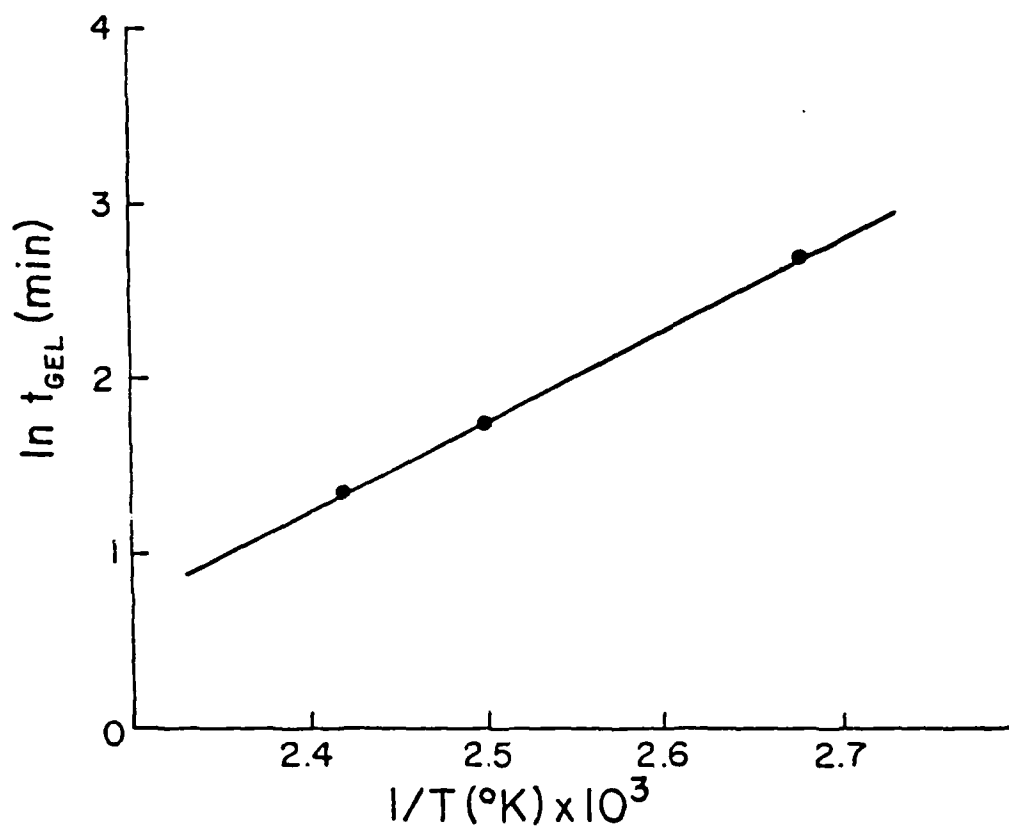
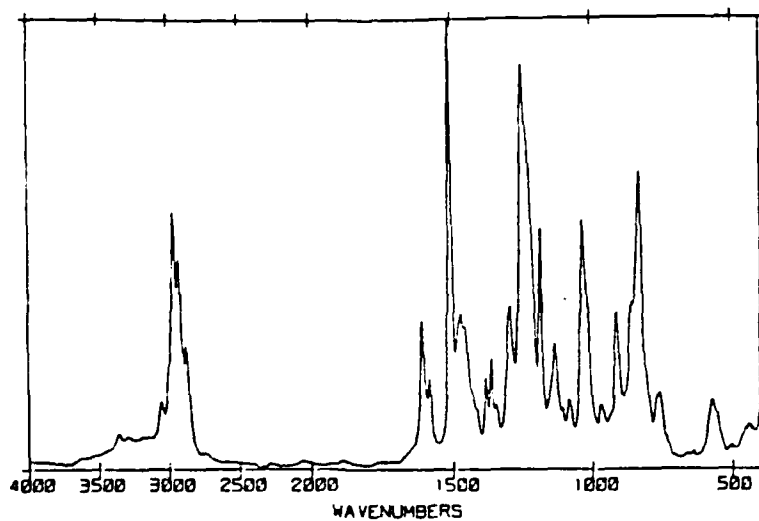
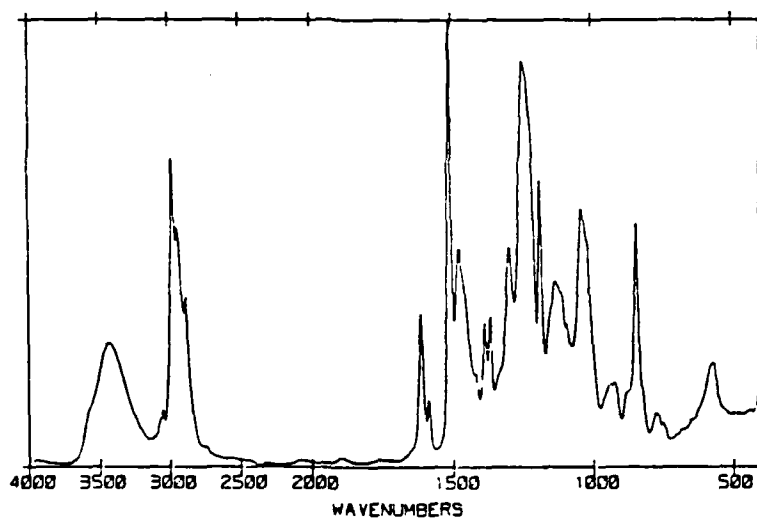


Figure 4. Arrhenius plot of logarithm time to gelation versus reciprocal temperature from TBA results.



"Freshly Mixed"



"Partially Cured"

Figure 5. Infrared spectra of freshly mixed and partially cured resin specimens.

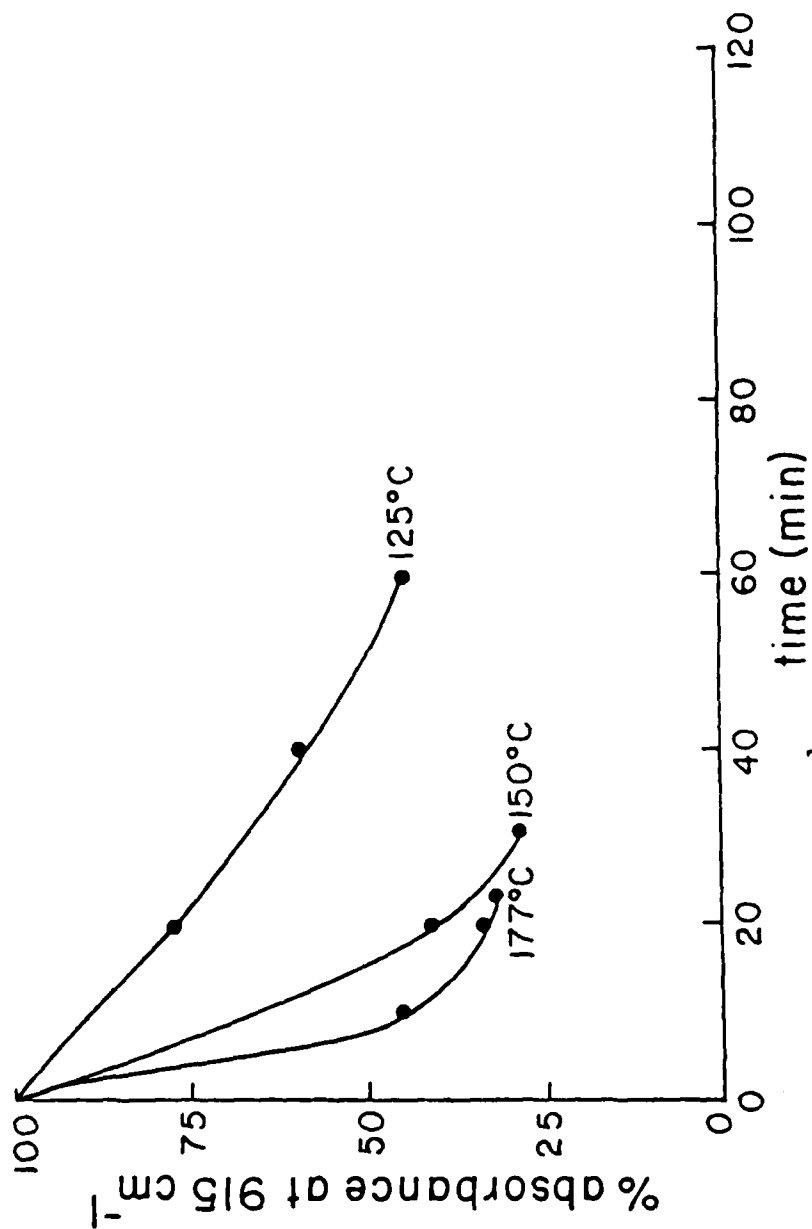


Figure 6. Absorbance at 915 cm⁻¹ versus time plot for the freshly mixed condition.

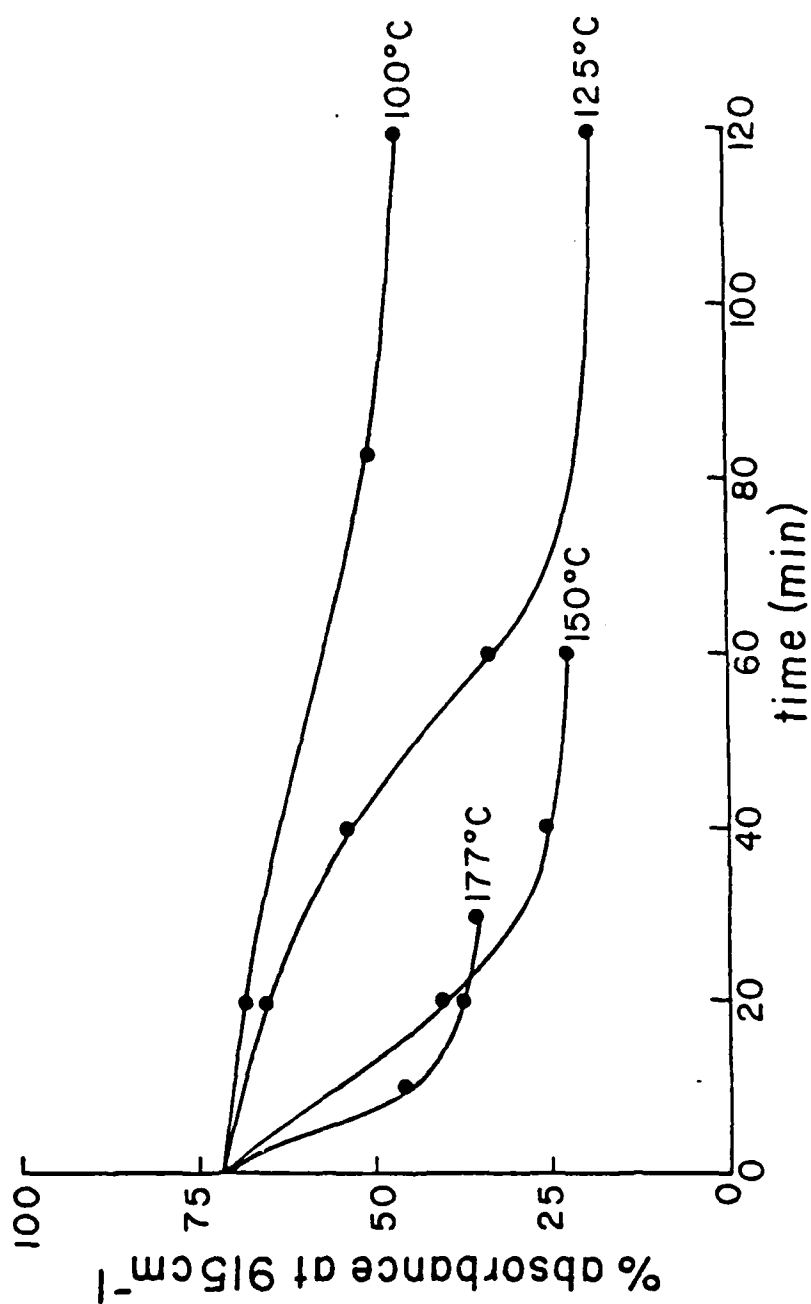


Figure 7. Absorbance at 915 cm⁻¹ versus time plot for the B-staged condition.

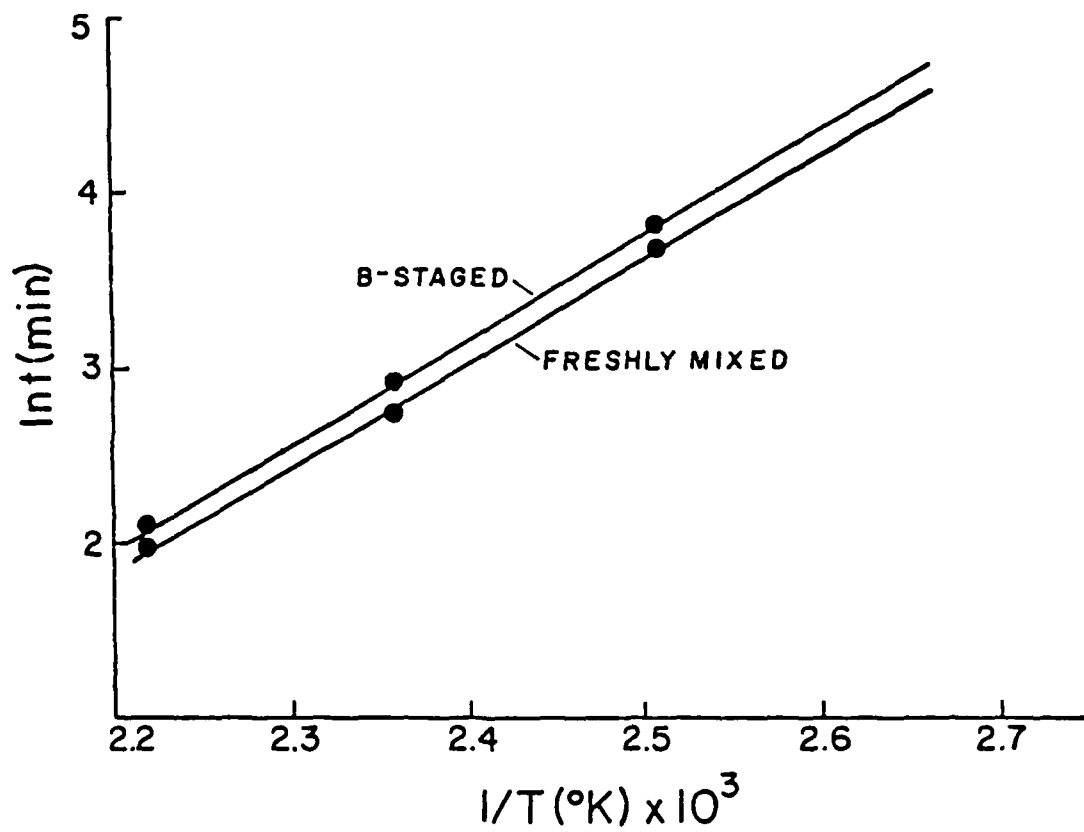
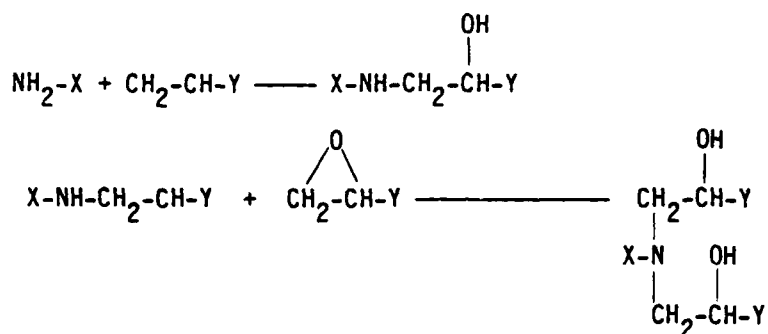


Figure 8. Arrhenius plot of logarithm time to 49% conversion versus reciprocal temperature from FT-IR results.

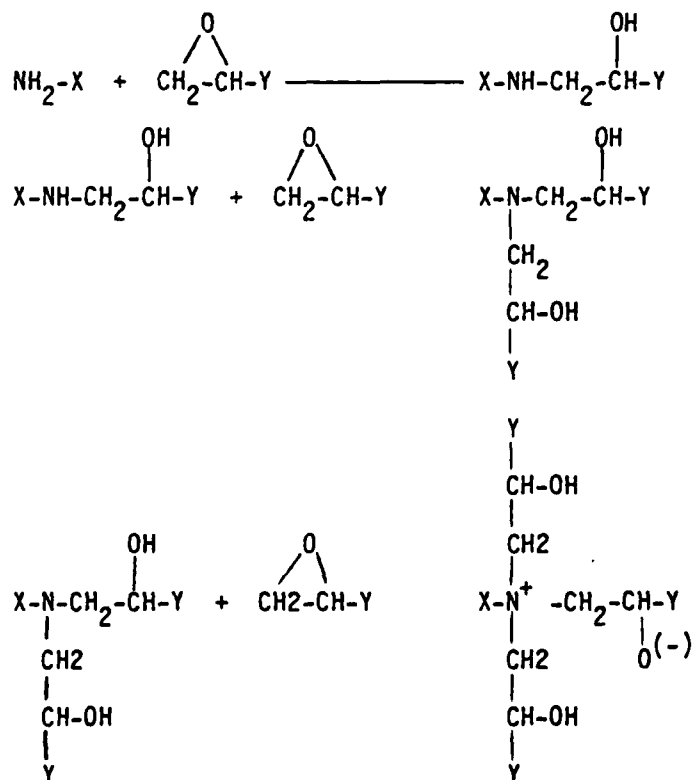
APPENDIX

The following mechanisms have been proposed as possible schemes for the amine-cure of epoxy resins (4).

Scheme I: (Simple Amine Addition)

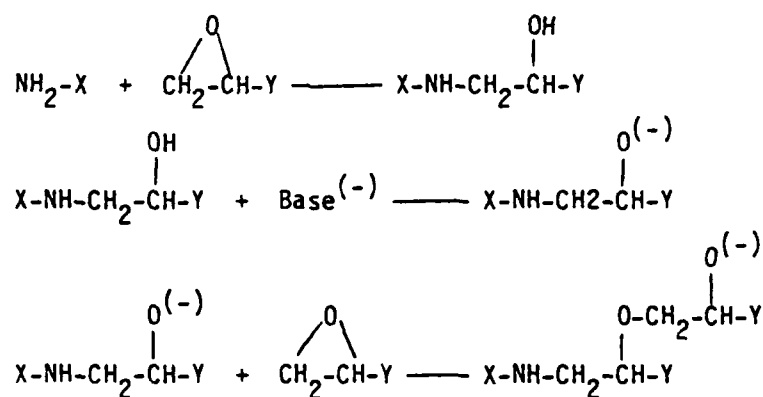


Scheme II: (Zwitterion Initiated Homopolymerization)



(The relatively stable Zwitterion may continue to add epoxide groups and thus initiates homopolymerization.)

Scheme III: (Alkoxide Ion Addition)



Scheme I is favored for a stoichiometric mix of amine and epoxy with *no* accelerator. With excess epoxide groups, oligomerization involving the hydroxyl groups has been shown to be possible (5). Schemes II and III become more probable with the introduction of an accelerator.

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